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(54) Title: USE OF A BETAINE SURFACTANT TOGETHER WITH AN ANIONIC SURFACTANT AS A DRAG-REDUCING AGENT

(57) Abstract

A combination of at least one betaine surfactant having a saturated or unsaturated alkyl or acyl group having 10-24 carbon atoms, preferably 14-24 carbon atoms, and an anionic surfactant having the general structure: R_1-B where R_1 is a hydrocarbon group with 10-24 carbon atoms and B is a group (a) or a group (b), in which M is hydrogen or a cationic, preferably monovalent group in a proportion between the betaine surfactant and the anionic surfactant of from 20:1 to 1:2, preferably from 10:1 to 1:1, reduces the flow resistance between a flowing water-based liquid system and a solid surface.

$$\begin{matrix} O \\ \parallel \\ -S-OM \\ \parallel \\ O \end{matrix} \quad (a) \qquad \begin{matrix} O \\ \parallel \\ -O-S-OM \\ \parallel \\ O \end{matrix} \quad (b)$$

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USE OF A BETAINE SURFACTANT TOGETHER WITH AN ANIONIC SURFACTANT AS A DRAG-REDUCING AGENT

The present invention relates to the use of a betaine surfactant together with an anionic, surface active sulphate or sulphonate in a water-based system for reducing the flow resistance between a solid surface and the water-based liquid system.

Surfactants with the ability to form extremely long, cylindrical micelles have, in recent years, attracted a great interest as drag-reducing additives to systems with circulating water, especially those destined for heat or cold distribution.

An important reason for this interest is that, although one desires to maintain a laminar flow in the conduits, one wishes at the same time to have turbulence in the heat exchangers to achieve therein a high heat transfer per unit area.

As may easily be understood, fibres or chain polymers are unable to provide this double function which, however, can be achieved with thread-like micelles, since the flow rate (the Reynold's number) usually is much higher in the heat exchangers than in the conduit.

The thread-like micelles are distinguished by operating in a fairly disorderly fashion at low Reynold's numbers (below 10^4), having no or only a very slight effect on the flow resistance. At higher Reynold's numbers (above 10^4), the micelles are paralleled and result in a drag reduction very close to that which is theoretically possible. At even higher Reynold's numbers (e.g. above (10^5), the shear forces in the liquid become so high that the micelles start to get torn and the drag-reducing effect rapidly decreases as the Reynold's number increases above this value.

The range of Reynold's numbers within which the surface-active agents have a maximum drag-reducing effect is heavily dependent on the concentration, the range increasing with the concentration.

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By choosing the right concentration of surface-active agents and suitable flow rates in tubings and heat ex- changers, it is thus possible to establish a laminar flow in the tubes and turbulence in the heat exchangers. Thus, the dimensions of both the tubes and the exchangers can be kept at a low level, or the number of pump stations, and conse- quently the pump work, can alternatively be reduced while retaining the same tubular dimensions.

The surface active agents most commonly used as drag- reducing additives to circulating water systems for heat or cold distribution are of the type represented by alkyltrimethyl ammonium salicylate, wherein the alkyl group is a long alkyl chain which has 12-22 carbon atoms and which may either be saturated or contain one or more double bonds.

This type of surface-active agent functions satis- factorily already at a concentration of 0.5-2 kg/m^3, but is degraded very slowly, both aerobically and anaerobically, and further is highly toxic to marine organisms.

Since heat-distribution systems for small houses usu- ally suffer from important leaks (it is estimated that in one year 60-100 per cent of the water leaks out), it follows that the added chemicals end up in the ground water and in various fresh-water recipients. This combination of low bio- degradability and high toxicity is a fundamental criterion for a product injurious to the environment.

Thus there is a general demand for surface-active agents which are less harmful to the environment but which have the same excellent ability as the quaternary ammonium compounds described above to reduce the flow resistance in circulating water systems.

In the US Patent 5 339 855 it is described that al- koxylated alkanolamides with the general formula

$$RCNH(A)_nH$$
$$\overset{\|}{O}$$
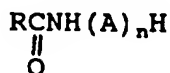
wherein R is a hydrocarbon group having 9-23 carbon atoms, A is an alkyleneoxy group having 2-4 carbon atoms and n is 3- 12, are capable of forming long cylindrical micelles in

water and thus reduce the drag in water-based system.

These products are easily degradable and function ex-
cellently in deionized water especially at low temperatures.
However, the drag-reducing effects are hampered in hard
water and by the presence of high amounts of electrolytes.
Further the temperature range for their optimal drag-
reducing effect will be rather narrow, sometimes as small as
10°C.

It has now surprisingly been found that essential
improvments is achieved by the use of at least one betaine
surfactant having a saturated or unsaturated alkyl or acyl
group with 10-24, preferably 14-24 carbon atoms in combina-
tion with an anionic surfactant having the general structure

$$R_1-B$$

where R_1 is an hydrocarbon group with 10-24 carbon atoms and

B is a group $-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}OM$ or a group $-O\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}OM$, in which M is a cat

ionic, preferably monovalent group, in a proportion between
the betaine surfactant and the anionic surfactant of from
20:1 to 1:2, preferably within 10:1 to 1:1, for producing a
water-based liquid system with low flow resistance between
the flowing water-based liquid system and a solid surface.
The betaine surfactant has preferably the general formula

$$R-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_2COO^- \qquad (I)$$
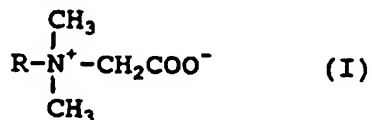
where R is the alkyl group or the group $R'NC_3H_6-$ where R' is
the acyl group. The hydrophobic group R_1 can be aliphatic or
aromatic, straight or branched, saturated or unsaturated.
The cationic group B is suitably an alkali group like sodium
or potassium. By "water-based" is meant that at least 50% by
weight, preferably at least 90% by weight, of the water-
based liquid system consists of water. Both the betaine sur-
factant and the anionic surfactant are readily degradable
and the combination gives an excellent drag reducing effect
within a wide temperature range. Thus, the drag-reducing

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additives may be used in a cooling media at temperatures below 30°C, when, for example using betaine surfactants, where the alkyl or acyl group has 14-16 carbon atoms, and in a heat-transfer medium at a temperature in the range of 50-120°C, when, for example using betaine surfactants where the alkyl or acyl group contains 18 carbon atoms or more. The mixtures according to the invention can also tolerate hard water and electrolytes which may be added e.g. as corrosion inhibitors. The carbon numbers of the hydrophobic groups R, R' and R_1 will determine the useful temperature range for the mixture so that high carbon numbers will give products suitable for high temperatures.

Furthermore, the betaine and anionic surfactants are suitably chosen in such a manner that the crystallization temperature for the combination is suitably below the lowest temperature for which the water-based system is intended.

The total amount of the betaine surfactant and the anionic surfactant may vary within wide limits depending on the conditions but is generally 0.1-10 kg/m^3 of the water-based system.

The solution of the betaine and anionic surfactant is especially suited for use in water-based systems flowing in long conduits, e.g. circulation water systems for heat and cold distributions.

The betaine surfactant can be produced by reacting a N-alkyl-N, N-dimethylamine or a N'-acyl-N,N-dimethyl-1,3 di-aminopropane with Na-chloroacetate at 70-80°C and a constant pH-value of 9.5 in a medium of a lower alcohol or water. To obtain a good drag reducing effect it is essential that the amount of the amine reactant in betaine product used is low. Preferably it should be lower than 5% by weight and most preferably lower than 2% by weight of the betaine surfac-tant. If a low chloride content in the product is necessary the reaction can preferably be made in isopropanol with the lowest water content possible, whereby the sodium chloride formed in the reaction will crystallize out of the product and may be removed by filtration or centrifugation.

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Another route to a chloride-free product is to quaternize the amine reactant with ethylene oxide and an acid catalyst and then dehydrogenate the resulting product to the desired betaine surfactant. The group R and R' in formula I can suitably be tetradecyl, hexadecyl, octadecyl, oleyl, rape seed alkyl and tallow alkyl or the corresponding acyl group.

The anionic surfactants suitable for use in accordance with the invention are well-known products and so are also the production methods. Typical examples are aliphatic alkyl sulphates derived from fatty alcohols or synthetic alcohols, and alkyl arenesulphonates like decylsulphate, dodecylsulphate, cocoalkylsulphate, oleylsulphates, tallowsulphates and the corresponding sulphonates and dodecylbensensulphonates and hexadecylbensensulphonate.

The choice of the anionic surfactant will depend on the hardness, the salt content and the temperature of the water. In hard water alkylbensensulphonates are suitable due to the better solubility of their calcium salts.

A convenient way to determine the right proportion between the betaine surfactant and the anionic surfactant for a certain type of water is to make up a solution of e.g. 0.500 kg/m^3 of the betaine surfactant in the appropriate water in a glass beaker with a magnetic stirrer and keep the temperature in the middle of the intended temperature range for the system. This solution is then titrated with a solution of the anionic surfactant with a concentration of 10 kg/m^3 in deionized water until the originally formed vortex has disappeared.

The details of this procedure are described in more detail under the heading "Screening test".

Apart from the betaine and anionic surfactant, the water-based system may contain a number of conventional components such as rust-preventing agents, anti-freeze and bactericides.

The present invention will now be further illustrated with the aid of the following examples.

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Examples

The drag-reducing properties of the compositions and products according to the prior art have been tested according to two different methods, one rather simple procedure, which will be called the screening test, and one more elaborated streaming test, which will be called the loop test.

Screening test

A serie of 50 ml glass beakers of the same dimensions (65x35 mm) each containing a Teflon-covered cylindrical magnet (20x6 mm) were each filled with 40 ml test solution and then placed on a magnetic stirrer, a thermometer immersed to a depth of 15 mm, the stirrer started at full speed, 1400 rpm, and the depth of the vortex formed in the solution was recorded at various temperatures.

When no vortex could be detected (recorded as 0 mm), it is known by experience that this indicates good drag reducing properties.

If on the other hand no efficient additive was present, e.g. for pure water the vortex reached down to the stirring magnet and the result was recorded as 35 mm.

Loop test

Measurements were carried out in a 6 m tube loop consisting of two straight and stainless tubes (3 m each), one tube having an inner diameter of 8 mm and the other having an inner diameter of 10 mm. Water was pumped through the tube loop by a centrifugal pump, which was driven by a frequency-controlled motor for continuous adjustment of the flow rate, which was determined by a rotameter.

The straight parts of the tube loop had outlets which, with the aid of valves, could in turn be connected to a differential pressure gauge whose other side was all the time connected to a reference point in the tube loop. Further, the tube loop was heat-insulated, and the suction side of the pump was connected to a thermostatically controlled container with a volume of 20 l, to which the return flow from the tube loop was directed.

After the test compound had been added and the

aqueous solution had been thermostatically controlled, mea-
surements began at low flow rates, and the pressure differ-
ence from two points on the 10 mm tube and three points on
the 8 mm tube were measured for each flow rate. The pressure
differences thus measured were then converted into Moody's
friction factory Y and are shown in the examples as a func-
tion of the Reynold's number Re.

$$Y = 2D.P_{diff}/V^2.L.d$$

$$Re = D.V.d/u$$

D = tube diameter

V = flow rate

L = tube length over which the pressure difference
P_{diff} was measured

d = density of the liquid

u = viscosity of the liquid

The examples also state the corresponding Prandtl
number and Virk number. The former corresponds to the fric-
tion factor of water flow in turbulence, and the latter
corresponds to flow without turbulence, i.e. a laminar flow.

Example 1

A modified sea-water was prepared by dissolving 38 g
NaCl, 5 g $Ca(NO_3)_2 \cdot 4 H_2O$ and 5 g $MgSO_4$ to 1.00 litre of tap
water containing 8 ppm Ca^{2+}.

In 40 mls of the water described above 43 mg active
substance of N-hexadecyl betaine with the structure

$$CH_3(CH_2)_{15}-N^+(CH_3)_2-CH_2COO^-$$
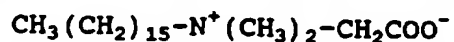
(in the following called C_{16}-betain) and 6.6 mg active sub-
stance of the sodium salt of a linear dodecylbenzenesulpho-
nate with the structure

$$C_{12}H_{25}-C_6H_4SO_3^-Na^+$$

(in the following called Na-LAS), were dissolved. This test
solution was kept in a 50 ml glass beaker which also con-
tained a 20 mm magnetic stirrer and was cooled down to +5°C
in a refrigerator and then tested at different temperatures
from 8 to 24°C. The depth of vortex formed in mm at the
stirrer speed of 1400 r.p.m. was measured. The following
results were obtained.

Temp. °C	Vortex, mm	Appearance
8	20	cloud
13	2	cloud
16	0	slight cloud
17.5	0	haze
19	1	clear
20	2	clear
22	3	clear
24	5	clear

From the results it is evident that the use of a alkyl chain having a length of 16 carbon atoms i.e. a C_{16}-instead of a C_{18}-betaine in combination with an anionic surfactant can be used for cold water applications.

Example 2

In 40 mls of deionized water 80 mg active substance of a C_{18}-betaine and 8 mg active substance of Na-LAS were dissolved. The structures of these compounds were the same as those given in Example 1 except that the C_{18}-betaine has an alkyl chain containing totally 18 carbon atoms. The test solution was tested in the same manner as in Example 1 at different temperatures from 30-90°C. The following results were obtained.

Temp. °C	Vortex mm
30	1
40	0
50	0
60	0
70	0
80	0
90	2

The solution was clear in the whole temperature range.

The screening test in Example 2 indicates that a combination of C_{18}-betaine and Na-LAS has a good drag-reducing effect in the temperature range 30-88°C.

Examples 3-5

The tests were performed according to the loop test method. Deionized water was used in these tests.

The composition of the drag-reducing agent was 85 parts of C_{18}-betaine and 15 parts of Na-LAS and 0.5 kg/m^3 of this mixture was added in Example 3 and 4 and 2.0 kg/m^3 in Example 5. The temperature was 50°C in Example 3, 85°C in Example 4 and 98°C in Example 5. The following results were obtained.

	Moody's friction factor x 10^3					
Reynolds number	6x10^3	10^4	2x10^4	5x10^4	8x10^4	2x10^5
Prandtl number	36	32	27	21	19	15
Example 3	36	20	16	21	18	15
Example 4	18	13	7	5	18	15
Example 5	36	28	29	21	16	13
Virk number	15	11	7	5	4	2.8

All values are calculated from measurements in the 8 mm tube. From these three loop tests it may be concluded that the combination of N-alkylbetaine and anionic surfactant used has good drag-reducing effect at least in the temperature range 50-85°C and that this effect decreases substantially somewhere between 85 and 98°C. This results are in good agreement with the results from the screening tests in Example 2.

Example 6

A test solution was prepared by dissolved 60 mg active substance of C_{18}-betaine and 19 mg of sodium lauryl sulphate in 30 mls of deionized water. The pH value of the solution was 9.5. In the screening test this solution showed no vortex formation from 30°C to 87°C.

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Example 7

15 mg active substance of an amide between rape seed acids and N,N-dimethylpropylenebetaine having the structure of

$$RCONHCH_2CH_2CH_2N^+(CH_3)_2CH_2COO^-$$

where RCO is derived from the fatty acids of rape seed oil. The fatty acid containing 60% by weight of oleic acid, 20% by weight of linoleic acid, 9% by weight of linolenic acid, 3% by weight of erucic acid and the rest mainly palmitic and stearic acids, was dissolved in 30 ml of deionized water together with 1.2 mg active substance of sodiumdodecylbenzenesulphonate. The pH of the solution was adjusted with NaOH to 9.8 and the speed of the magnetic stirrer to 1100 r.p.m.. The solution was heated slowly from room temperature up to 80°C and the vortex depth observed in accordance with the screening test.

The following results were obtained.

Temp, °C	20	25	30	35	40	45	50	55	60	75	80
Vortex mm	35	20	5	5	3	0	0	0	0	1	10

These results show that this composition performs well as drag-reducing agent in the interval 30-75°C.

C L A I M S

1.   Use of at least one betaine surfactant having a saturated or unsaturated alkyl or acyl group having 10-24, preferably 14-24 carbon atoms, in combination with at least one anionic surfactant having the general structure

$$R_1\text{-}B$$

where R_1 is a hydrocarbon group with 10-24 carbon atoms and

B is a group $-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}OM$ or a group $-O\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}OM$, in which M is hydrogen

or a cationic, preferably monovalent group in a proportion between the betaine surfactant and the anionic surfactant of from 20:1 to 1:2, preferably in the range from 10:1 to 1:1 for producing a water-based liquid system with reduced flow resistance between the flowing water-based liquid system and a solid surface.

2.   Use of at least one betaine surfactant of the general formula

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{R\text{-}N^+\text{-}CH_2COO^-}} \qquad (I)$$
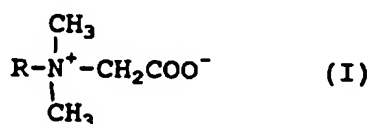
where R is the alkyl group or the group $R'NC_3H_6-$ where R' is the acyl group.

3.   Use as claimed in claim 2, **characterized in**, that the crystallization temperature for the mixture is below the lowest temperature for which the water-based system is intended.

4.   Use as claimed in claim 1, 2 or 3, **characterized in**, that the water-based system is a heat-transfer medium with a temperature in the range of 50-120°C.

5.   Use as claimed in claim 1, 2 or 3, **characterized in**, that the water-based system is a cooling medium with a temperature below 30°C.

6.   Use as claimed in any one of claims 1-5, **characterized in**, that the mixture of betaine surfactant and anionic surfactant is added in an amount of 0.1-10 kg/m^3 of the

water-based system.

7.   Use as claimed in any one of claims 1-4 and 6, **characterized in**, that the alkyl group contain 18-24 carbon atoms.

8.   Use as claimed in claim 7, **characterized in**, that the alkyl group contains 18-22 carbon atoms and one or two double bonds.

9.   Use as claimed in any one of claims 1-4 and 6, **characterized in**, that the acyl group contain 18-24 carbon atoms.

10.   Use as claimed in claim 9, **characterized in**, that the acyl group contains 18-22 carbon atoms and one or two double bonds.

11.   Use as claimed in any one of claims 1-3 and 5-6, **characterized in**, that the alkyl group contains 14-16 carbon atoms.

12.   Use as claimed in claims 1-3 and 5-6, **characterized in**, that the acyl group contain 14-16 carbon atoms.

13.   Use as claimed in any one of claims 1-12, **characterized in**, that R_1 is an alkylbenzene group and B is a sulphonate group.

14.   Use as claimed in any one of claims 1-12, **characterized in**, that R_1 is an alkyl group and B is a sulphate group.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C10M173/02   C09K3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C10M   C09K   F17D   F15D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9509 Derwent Publications Ltd., London, GB; Class A25, AN 95-063964 XP002007466 & JP,A,06 340 888 (NIPPON OILS & FATS CO LTD) , 13 December 1994 see abstract ---	1-14
P,A	WO,A,95 11288 (BEROL NOBEL) 27 April 1995 see claims 1-9 ---	1-14
A	EP,A,0 091 086 (HOECHST AKTIENGESELLSCHAFT) 12 October 1983 see claim 1 --- -/--	1-14

| X | Further documents are listed in the continuation of box C. | | X | Patent family members are listed in annex. |

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 505 827 (G.D. ROSE) 19 March 1985 see column 6, line 17 - line 19 see column 3, line 27 - line 38; claims 1,4,11 ---	1-14
A	US,A,5 143 635 (J.C.O.C.C. YOUNG) 1 September 1992 see column 3, line 25 see column 3, line 33 - line 45 see column 4, line 3 - line 5 -----	1-14

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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9511288	27-04-95	SE-C-	500923	03-10-94
		CA-A-	2171558	27-04-95
		SE-A-	9303458	03-10-94
EP-A-91086	12-10-83	DE-A-	3212969	13-10-83
		CA-A-	1208421	29-07-86
		DE-A-	3377588	08-09-88
		JP-C-	1713048	27-11-92
		JP-B-	3076360	05-12-91
		JP-A-	58185692	29-10-83
US-A-4505827	19-03-85	NONE		
US-A-5143635	01-09-92	CA-A-	2009210	02-08-91